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## Improvement the Superconducting properties of $TlBa_2Ca_2Cu_{3x}Ni_xO_{9-\delta}$ superconducting compound by partial substitution of copper with nickel oxide on the

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### Abstract

In this study is presented the partial replacement of copper with nickel  $TlBa_2Ca_2Cu_{3x}Ni_xO_{9-\delta}$  superconductor with ( $x=0,0.2,0.4,0.6,0.8,1.0$ ). The samples were prepared in a solid state reaction method with a  $850\text{ }^\circ\text{C}$  sintering temperature for 24 hours. Structural of the samples were studied by using X-ray powder. The XRD analysis showed that a tetragonal diagram and polycrystalline structures with a majority phase 1223 and changes in nickel concentrations resulted in a change in the parameters of lattice parameters a, b, c axis c / a, mass density and Volume fraction. Four prop technique were used to test the electrical resistivity to determine the critical temperature at zero resistance  $T_{c(\text{offset})}$ . The best transfer temperature was obtained from the  $TlBa_2Ca_2Cu_{2.4}Ni_{0.6}O_{9-\delta}$  sample, which is equal to 134.6 Kelvin.

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*Keywords:* Electrical resistivity, superconductor, critical temperature

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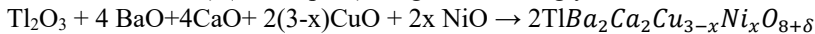
## 1. Introduction:

The phenomenon of superconductivity is obtained in different types of materials include elements such as tin, aluminum, types of various metal alloys, some semiconductors with high- doping and some ceramic compounds which have contained copper layers and oxygen contain. The last compounds are called "Cup rates, superconducting materials with high critical transmission temperatures, and the phenomenon of superconductivity is not obtained in noble metals such as gold and silver or in ferromagnetic metals [1]. The majority superconducting of materials are compounds and alloys and these are not pure elements, the transition temperature of the elements are different from the metal alloys and components, the higher temperature of the transition in fact is observed in compounds and alloys [2]. The electrical resistance of superconducting materials drops abruptly to zero when the temperature drops to a value below the critical transfer temperature. Above this level, the specific or resistive resistance has the usual formula.

The superconducting of system Tl-Ba-Ca-Cu-O had a critical temperature ( $T_c = 125\text{K}$ ) was discovered [3]. Discoveries of Tl-based superconducting system have not only set new  $T_c$  records with zero resistance up to 125K, but also have provided a new insight into the mechanism of high- $T_c$  oxide superconductor[4,5]. The compositional analysis and structure determination of the Tl-2223 have shown that the most interesting aspect of HTSc's chemical crystal is that for those who rely on Tl, there are not only variable numbers of Cu-O layers but also variable numbers of Tl-O layers [6], which provide the possibility of many compounds, in what is really A series of adoption without limit through the process of substitution and change interdependent elements. The entire string can be written:  $\text{Tl}_m\text{Ba}_2\text{Ca}_n\text{-1Cu}_n\text{O}_{m+2n+2}$  and  $\text{Tl}_m\text{Sr}_2\text{Ca}_n\text{-1Cu}_n\text{O}_{m+2n+2}$ [7].

## 2. Experimental:

The specimens were prepared in a solid state reaction using appropriate weights of high purity oxides ( $\text{Tl}_2\text{O}_3$ , BaO, CaO, CuO, NiO) (99.9% pure) weights accordingly for these chemical formulas:



Dry the Powdered under  $125^\circ\text{C}$  for 1.5h to get rid of Water vapor, and then all the reactants were weighed by a sensitive digital balance of four decimal places. The powders were mixed and grinded by a 6-hour spiral electric mixer for optimal homogenization and for accurate powders. The powders produced in the drying oven were dried under temperature ( $125^\circ\text{C}$ ) for 1.5h. The resulting powder mixtures were then compressed using a hydraulic piston under a pressure of 7 ton /  $\text{cm}^2$  for two minutes, in the form of tablets with a diameter of 1.5cm and a thickness of (0.25-0.25 cm.). The specimens were sintering in the normal atmosphere less than  $850^\circ\text{C}$  for 24 h and at a heating rate of  $5^\circ\text{C} / \text{min}$  to obtain a bonding material and to ensure optimal propagation between the atoms gradually. The specimens were cooled to a temperature of  $400^\circ\text{C}$  for four hours for annealing and then cooled to room temperature at the same rate. After the specimens were obtained, an XRD test was carried out to obtain the structural properties of the specimens. (80-10) degree has been the lattice parameters account (a, b, c) mathematically based on the law of Bagg diffraction in the X-ray analysis, then measured the density of the unit cell, density of mass  $d_m$  was calculated as explained in the references [8-11]. The proportions of phases formed in the specimen calculation based on the relationship [9]:

$$V_{ph} = \frac{\sum I^o}{\sum I^o + \sum I_1 + \sum I_2} * 100\% \quad (1)$$

The measurement of the electrical resistivity as a function of the temperature was done using the four point probe technique. The specimens were cooled using liquid nitrogen. Determination of the dielectric properties, which included the dielectric constant (real and imaginary), the  $\tan\delta$  loss and the alternating conductivity were calculated by calculating the capacitance (C) and conductivity (G) (LCR Meter) and frequency (50 Hz-5MHz) and according to the following relationships[12]:

$$\varepsilon' = Cd/A\varepsilon \quad \dots\dots\dots(2)$$

$$\epsilon'' = Gd/2\pi\rho\epsilon \dots\dots\dots(3)$$

$$\tan\delta = \epsilon''/\epsilon \dots\dots\dots(4)$$

$$\sigma_{ac} = 2\pi f\epsilon'' \dots\dots\dots(5)$$

The characteristics of the surface for specimens Roughness, Root mean square and Avg. Diameter were observed from the AFM examination [8].

### 3. Results and Discussions

The x-ray diffraction pattern of the specimens with (x=0,0.2,0.4,0.6,0.8and 1.0) is shows in figure (1). The results of the XRD analysis showed that all the specimens it have a crystalline tetragonal structure with a change in the intensity of the peaks and their positions. It shows an increase in the Tl-1223 peaks which indicates an increase in the rate of formation of the high phase and a decrease in the peaks of other low phases and impurities it can be produced defects in the internal structure of the crystal,a variation has also been in the structural properties of phase ratios, lattice parameter , c / a, and density, by increasing the high phase with increment of nickel concentration until x=0.6 , which showed a marked improvement in the rate of formation of the higher phase, where we noted in Table (2) , where the effect of the substitution process was positive for the formation of the higher phase .

Where the presence of nickel in the composition of the specimens had a direct impact on the increase in the formation of high phase (Tl-1223) with a decrease in the rest of the phases and impurities in different away and this can be attributed to the effect of growth with partial fusion or partial liquid phase, Which works on processing the defects in microscopic structures such as cracks in superconducting granules caused by mechanical deformities during the substitution process, which result in a change in the stability of the high phase[12].

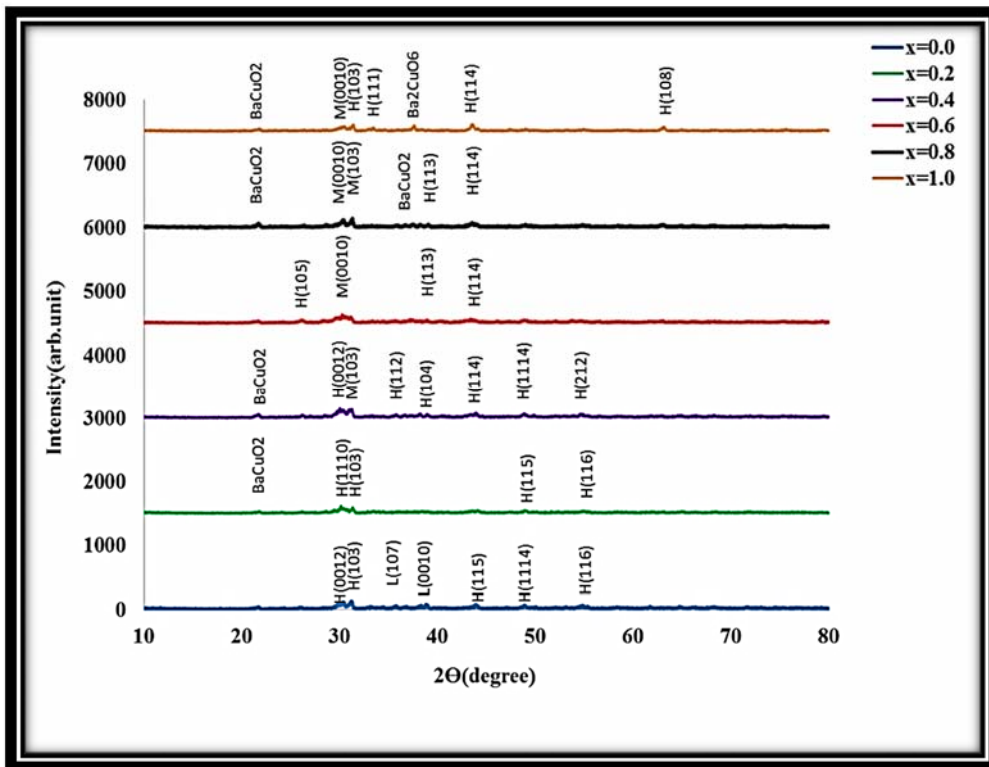


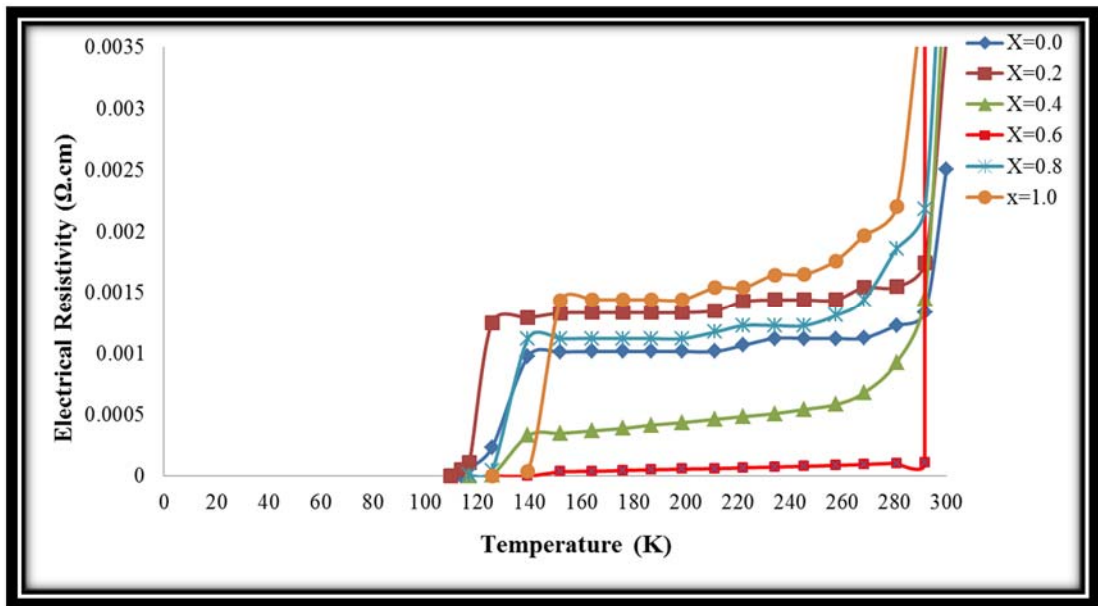
Fig. 1. X-ray diffraction analysis diagram of  $TlBa_2Ca_2Cu_{3-x}Ni_xO_{9.6}$  ( x=0, 0.2, 0.4, 0.6,0.8 and 1.0)

**Table 1.** The examination of X-ray diffraction

X	a=b (Å)	c(Å)	c/a ratio	v(Å) <sup>3</sup>	dm(gm/cm <sup>3</sup> )	V ph(1223)%	V ph(1212)%	V ph(1201)%	Vp impurities%
0	3.1464	15.1171	4.80457	149.6568	10.40618	71.2909	17.5337	6.2620	4.6242
0.2	3.4210	15.3458	4.485764	179.5956	8.662477	72.1082	4.6643	4.6643	12.8731
0.4	3.5357	15.5546	4.399299	194.4508	7.99241	74.6478	5.9859	14.9647	6.3380
0.6	3.5520	16.0433	4.516695	202.4136	7.670029	85.0467	15.5763	4.9532	4.6728
0.8	3.7023	15.6143	4.217459	214.0256	7.246355	60.2702	16.4864	18.6486	4.5945
1	3.9592	14.6648	3.703981	229.8746	6.739731	54.8455	28.7539	13.3120	3.5143

The change in the lattice parameters refers to the introduction of oxygen, which may be due to the effect of the environment surrounding the preparation conditions, which have a significant impact in the concentration of oxygen, which leads to change in the phases and lattice parameter of the superconducting compounds [13, 14].

In Figure (2), which represents the behavior of electrical resistivity as a function of the temperature of the specimens, where we note from the diagram that all the specimens were metal behavior in the region before ( $T_c$  offset), in which the specimen begins transition to superconducting state, there is an increase in the critical temperature of the specimen ( $x = 0.6$ ) compared to the critical temperature of the pure specimen, in which the nickel substitution can be considered the optimal substitution ratio as shown in Fig( 2 )and Table( 2), Where it has the highest percentage of the highest phase(T11223) and the highest temperature critical( $T_c$ ) for the specimen, which contains a small percentage of impurities, which can be counted the optimum specimen ( $x=0.6$ ) in this compound, as it has the highest proportion of the highest phase and the highest temperature is possible and may be attributed to this is access to substitution rates. And the substitution process can result in some additional charges being transferred into layers (CuO), which leads to some copper atoms being transferred from the oxidation state ( $Cu^{+2}$ ) to ( $Cu^{+3}$ ) and that this case is mixed parity lead to a significant improvement in the superconductivity. Note that nickel substitution leads to an increase in  $T_c$  to 134.6K ( $x = 0.6$ ) due to the increase of the c axis which leads to an increase in the CuO layer. The results are almost identical to those mentioned in reference [8-9]



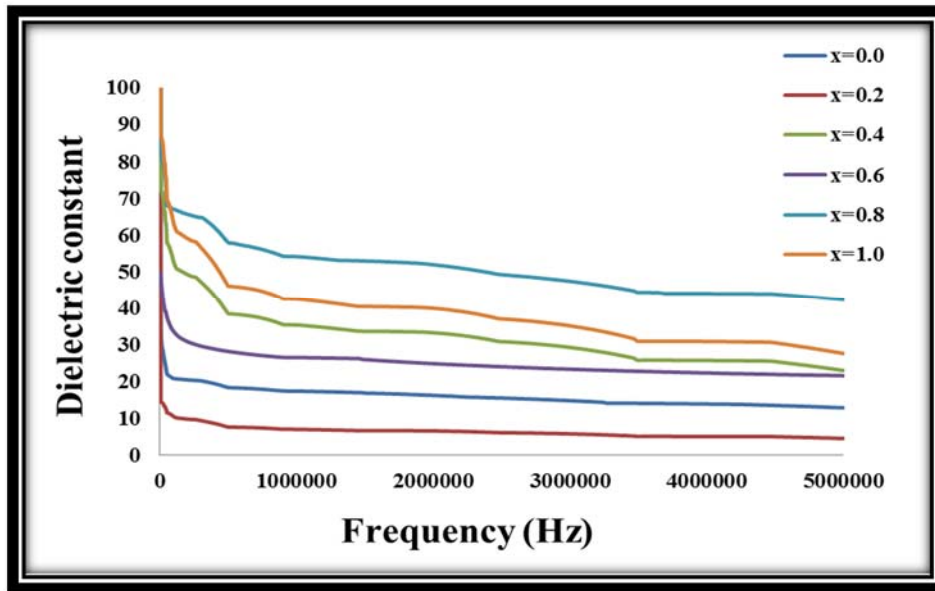
**Fig. 2.** Electrical resistivity v.s temperature

**Table 2.** The volume fraction ,the critical transition temperature and oxygen content  $\delta$

X	V <sub>ph</sub> (1223)%	V <sub>ph</sub> (1212)%	V <sub>ph</sub> (1201)%	V <sub>ph</sub> impurities%	T <sub>C(OFF)</sub> (K)	T <sub>C(ON)</sub> (K)	$\Delta T_C$ (K)	T <sub>C(mid)</sub> (K)	E <sub>g</sub> (eV)	$\delta$
0	71.2909	17.5337	6.2620	4.6242	117	125.6	8.6	121.3	0.0368	0.0464
0.2	72.1082	4.6643	4.6643	12.8731	123	128	5	125.5	0.0381	0.1157
0.4	74.6478	5.9859	14.9647	6.3380	123.5	130	6.5	126.6	0.0385	0.1137
0.6	85.0467	15.5763	4.9532	4.6728	129	140.2	11.2	134.6	0.0409	0.1253
0.8	60.2702	16.4864	18.6486	4.5945	113	126.2	13.2	119.6	0.0363	0.1333
1	54.8455	28.7539	13.3120	3.5143	113.5	116.5	3	115	0.0349	0.1173

In this work, we measured the dielectric properties of the specimens on the (LCR-Meter) and the frequency (50 Hz-5MHz) at room temperature. All CuO compounds are dielectric. By substituting certain atoms in the cell unit, these materials can behave in a metallic and can become superconducting. The transition temperature strongly depends on the intensity of the cases at the Fermi level. This factor has a strong effect on Vaccination of ceramic compounds with other seeds, which are different in size to provide them with extra electrons or gaps that they provide to become superconducting material [15].

The general behavior of dielectric constant in solid materials its decrease by increasing the frequency of the electrolytic field. In physical and polar matter, the primary value of the real dielectric constant is high, but with increasing frequency the value starts to decrease. This is due to the lateness response of dipoles to follow the change in the electric field at high frequencies.



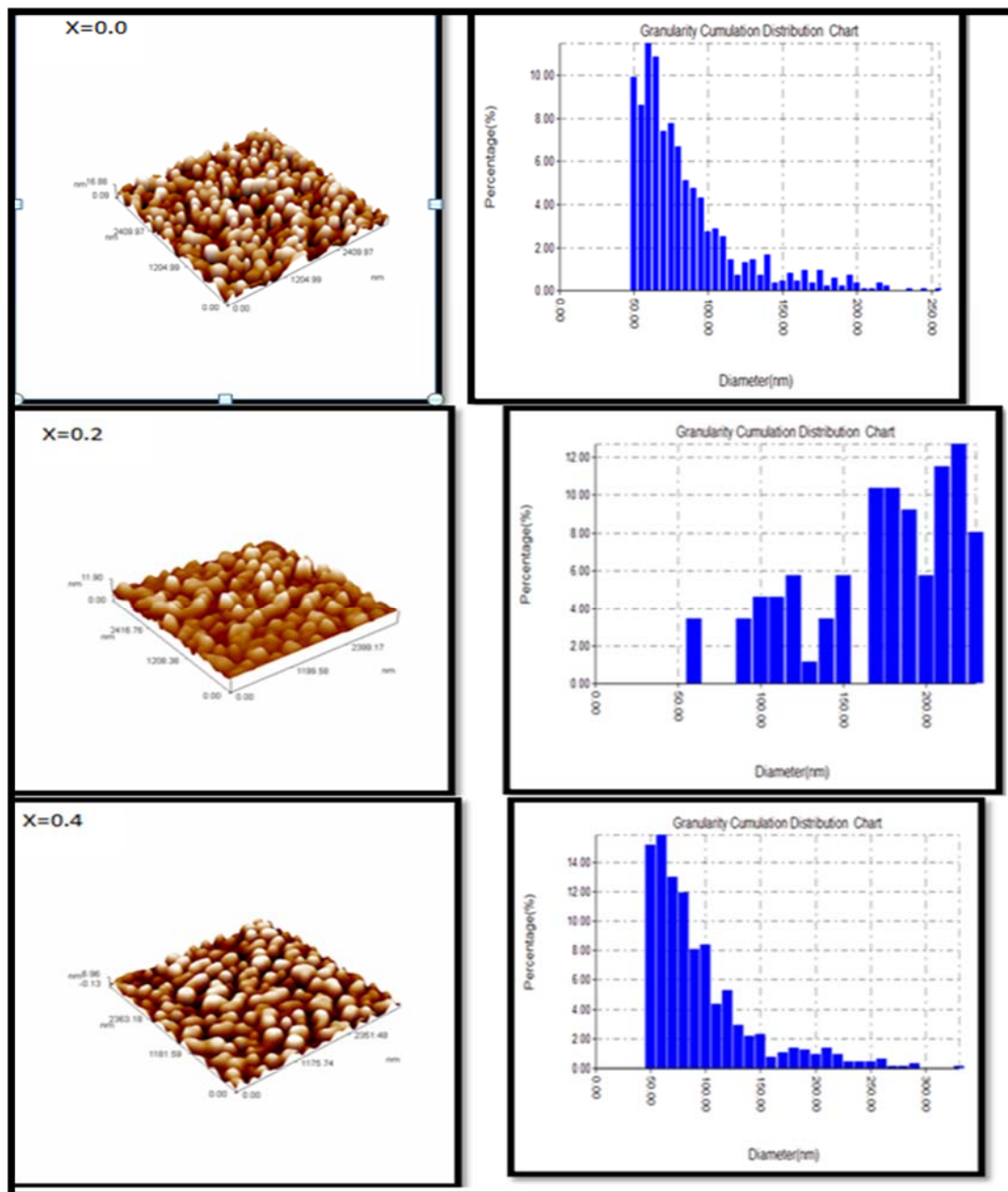
**Fig. 3.** Dielectric constant ( $\epsilon$ ) versus frequency

**Table 3.** The dielectric constant,  $\tan\delta$  loss and the alternating conductivity

X	$TlBa_2Ca_nCu_nO_{2n+3-\delta}$							
	$\epsilon$ At (50 Hz)	$\epsilon$ At (5MHz)	$\epsilon$ At (50 Hz)	$\epsilon$ At (5MHz)	$\tan\delta$ At (50 Hz)	$\tan\delta$ At (5MHz)	$\sigma_{a.c}$ ( $\Omega.cm$ ) <sup>-1</sup> At (50 Hz)	$\sigma_{a.c}$ ( $\Omega.cm$ ) <sup>-1</sup> At (5MHz)
0.0	27.784	12.557	286.57	0.4922	2.244	0.0540	$7.96 \cdot 10^{-9}$	$6.02 \cdot 10^{-6}$
0.2	14.436	4.022	12.448	0.3029	0.2432	0.0526	$2.04 \cdot 10^{-10}$	$1.09 \cdot 10^{-6}$
0.4	37.559	0.0009	67.409	2.277	0.3031	0.055	$8.14 \cdot 10^{-10}$	$1.63 \cdot 10^{-6}$
0.6	4385.58	2131.14	110.309	3.727	1.562	0.1079	$2.05 \cdot 10^{-7}$	$6.21 \cdot 10^{-6}$
0.8	675.565	40.563	93.336	3.153	1.177	0.0267	$1.94 \cdot 10^{-9}$	$1.27 \cdot 10^{-5}$
1.0	84161.24	802.152	86.669	2.928	0.5786	0.0399	$3.86 \cdot 10^{-7}$	0.00016

Figure(4) represent AFM images 3D of  $TlBa_2Ca_2Cu_3-xNi_xO_{9-\delta}$ , superconductor compounds with  $x=(0.0, 0.2, 0.4, 0.6, 0.8, \text{and } 1.0)$ .

It has been observed that there is an imbalance, and areas of high density and low dimensions of nanometers differ from one location to another within the sample. The size of the crystal, the roughness of the surface and the average diameter shown in Table (4) show that each sample contains a homogeneous and smooth crystalline crystal and gives the best value for the nano size is 81.86 nm at  $x = 0.6$ .



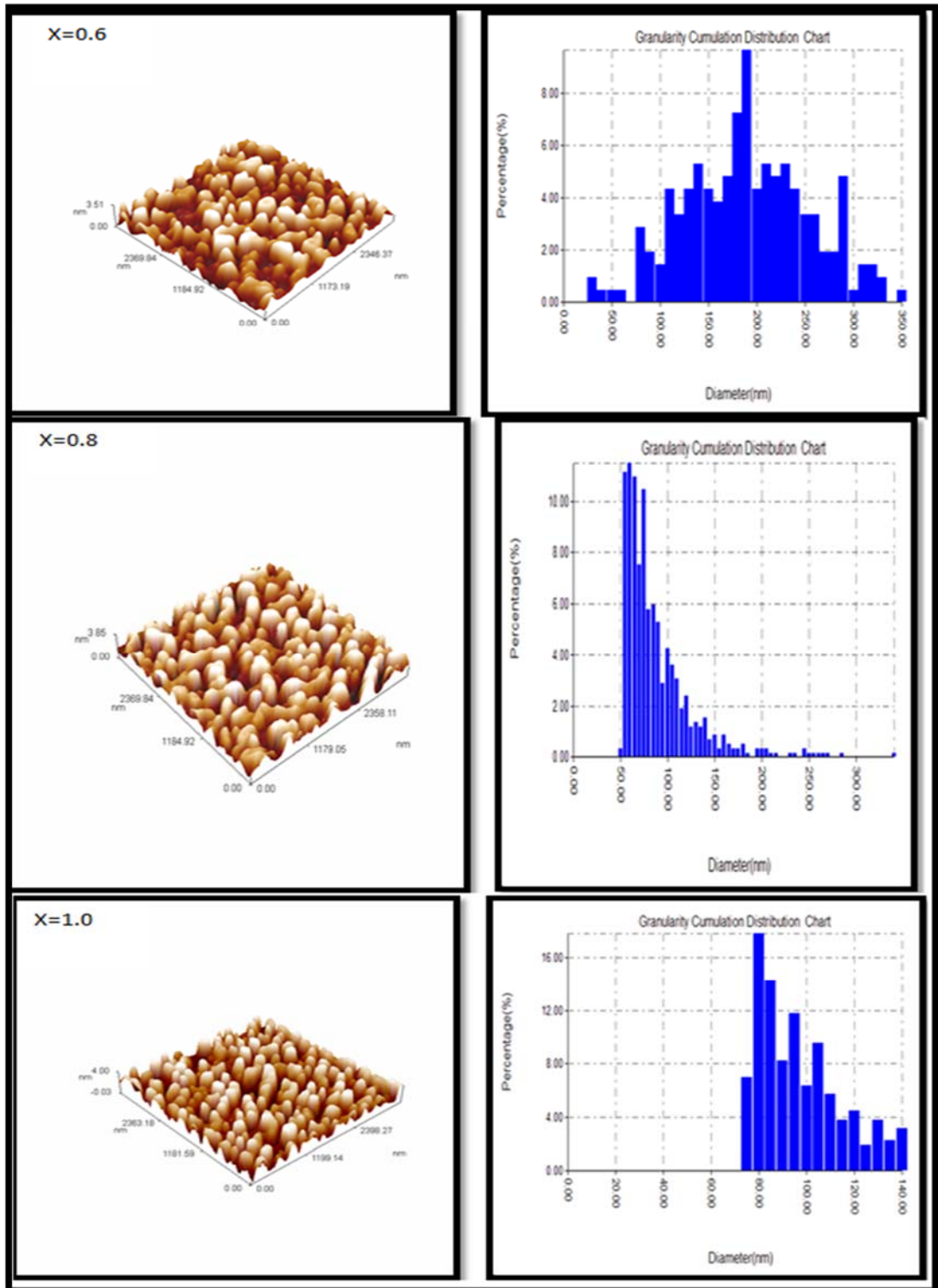


Fig. 4. AFM testing results.



**Table 4.** The Values of average surface roughness, Crystal size and Avg. Diameter in 2D for  $TlBa_2Ca_2Cu_{3-x}Ni_xO_{9.8}$ 

x	Crystal size(nm)	Roughness (nm)	Root mean square(nm)	Avg. Diameter(nm)
0	198.7377	4.26	4.9	185.08
0.2	103.7594	1.46	1.83	89.84
0.4	155.6031	1.83	2.1	167.21
0.6	47.31678	0.743	0.868	81.86
0.8	244.4281	0.935	1.08	86.54
1.0	212.9885	0.935	1.09	94.95

#### 4. Conclusions:

In this research, specimens were prepared for the superconductor compound  $TlBa_2Ca_2Cu_{3-x}Ni_xO_{9.8}$  by a method of solid state reaction and the structural tests were conducted. The results showed that the compound had a tetragonal structure the critical temperature of these specimens was determined through four point probe technique the highest critical temperature when  $x=0.6$  equal to 134.6 K and  $\delta=0.1253$  and we observed increment of c values until  $x=0.6$  then be decrease. the dielectric properties are directly decreasing with increasing the frequency from (50Hz) to (5MHz) with Ni content. The characteristics and information of the surface specimens are recorded through the examination of AFM then we found the best specimen when  $x=0.6$  the Avg. Diameter equal 81.86nm.

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